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"RIGID ROD MOLECULES AS LIQUID CRYSTAL THERMOSETS"

BY

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# Rigid Rod Molecules As Liquid Crystal Thermosets (LCT's)

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Rigid rod molecules endcapped with conventional crosslinking groups such as maleimide and nadimide were prepared and studied by differential scanning calorimetry and hot stage polarized light microscopy. Nematic liquid crystalline phases were identified in several of the new monomers. Thermally induced polymerization occurred in the nematic phase region and resulted in retention of the nematic texture in the final crosslinked solid. In many cases, isotropization was not observed at normal heating rates due to crosslinking and solidification in the nematic phase.

In 1975, Roviello and Sirigu reported on the preparation of polyalkanoates that melted into anisotropic phases (1). These mesophases were quite similar to those of conventional low molecular weight liquid crystals. Since this initial report, there has been considerable interest in liquid crystalline polymeric materials from both an academic and industrial

viewpoint. The initial motivation for the development of liquid crystalline polymers from the industrial viewpoint was largely due to the pursuit of high tensile property fibers. Polymers that exhibit liquid crystalline order in solution or in the melt can transfer a high degree of molecular orientation to the solid state which can lead to excellent mechanical properties (2). The technology of spinning rodlike aromatic polyamides from anisotropic solutions led to the first commercial product based on this idea. Subsequently, melt processing of liquid crystalline polyesters was also reported (3). Currently, there are at least three commercial thermotropic liquid crystalline polymers that can be used in a wide variety of thermoplastic polymer applications (4).

The field of thermoset polymers is an area of polymer science which has not yet been widely integrated with liquid crystal polymer research. It is interesting to note that Finkelmann et al. (5) reported on the formation of crosslinked elastomeric liquid crystalline networks in 1981. Although the general concept of a liquid crystal thermoset (LCT) has been addressed, very few physical or mechanical properties have been reported (6-10). It was claimed that these materials exhibited very low shrinkage upon curing but quantitative information was not disclosed. We have initiated an investigation to prepare and evaluate liquid crystal thermosets as high performance composite matrix materials. In this report, we present our preliminary results on the synthesis and characterization of both ester and amide based materials developed from the LCT concept.

## Experimental

Differential scanning calorimetry (DSC) was performed using a Perkin-Elmer DSC-2C at heating rates ranging from 20 °C min<sup>-1</sup> to 40 °C min<sup>-1</sup> under an argon atmosphere. Infrared (IR) spectra were recorded with a Perkin-Elmer 283 spectrophotometer using KBr pellets. Proton (<sup>1</sup>H) nuclear magnetic resonance (NMR) spectra were recorded using a JEOL PMX60SI NMR spectrometer at 60 MHz. All of the monomers synthesized for this study showed satisfactory spectra and elemental analyses.

The maleimide, nadimide, and methyl nadimide endcaps were prepared by reacting the appropriate anhydride and p-aminobenzoic acid in acetone at room temperature to yield

the corresponding amic acids. The amic acids were cyclodehydrated using acetic anhydride in the presence of sodium acetate according to the method of Rao (11). The endcaps were then treated with oxalyl chloride according to the method of Adams and Ulich (12) to yield the acid chlorides.

2,2'-Dimethyl-4,4'-diamino-1,1'-biphenyl dihydrochloride was obtained from Professor Lorraine Deck at the University of New Mexico and used as received. Maleic anhydride was obtained from Eastman Kodak and p-aminobenzoic was obtained from National Starch. The other anhydrides, diols, and reagents were purchased from Aldrich Chemical. All reagents were used without further purification. The monomers were synthesized via a Schotten-Baumann type procedure using the appropriate acid chloride endcap and diamines or diols. Triethylamine was used as a scavenger for HCl. The monomers were recrystallized from appropriate solvents in yields of approximately 70 %.

Solubilities were determined by placing the monomers in the appropriate solvents at five or ten percent (w/w) increments. Mild heating was used in some cases and the solutions were allowed to cool to room temperature. A positive room temperature solubility was recorded if the monomer did not recrystallize after sitting overnight at room temperature. The maximum room temperature solubilities for the monomers in Table 1 are within the ranges given in the table.

## Results and Discussion

One possible version of the LCT concept involves the design and preparation of new monomers consisting of a rigid rodlike central unit, a characteristic of conventional liquid crystals, capped at both ends with well known crosslinking groups. The crosslinking groups were chosen from the common functionalities used for thermoset materials such as epoxy, maleimide, acetylene, etc. This concept is shown schematically in Figure 1. In the present study, the results on maleimide, nadimide, and methyl nadimide endcapped monomers are reported. In order to design materials that would also possess high thermal stability, it was decided to construct the rigid rodlike portion of the molecule from aromatic amide and ester units. This simple design could, of course, lead to rather intractable materials, particularly in

the case of the aromatic amides, unless measures are taken to improve the tractability of these monomers. There are several known methods to improve the tractability of wholly aromatic liquid crystalline polymers. These methods attempt to disrupt the crystalline order of the p-linked chain without affecting it to such a degree that liquid crystallinity is lost. The techniques used to reduce melting points or improve solubilities have been reviewed (13,14) and include the use of bent and swivel monomers, flexible spacers, and bulky ring substituents. One of the structural modifications that produced dramatic improvements in melting points and solubilities was reported by Gaudiana et al. (15). The specific structural modification responsible for the improvements was the 2,2'-disubstituted 4,4'-biphenylene moiety. This substitution pattern forces noncoplanarity of the phenyl rings while maintaining the rodlike conformation of the backbone. The intermolecular interactions were also greatly affected. In the present work, a series of amide monomers employing the 2,2'-disubstituted 4,4'-biphenylene unit were prepared to determine if this modification could sufficiently reduce the intermolecular attractive forces to produce low molecular weight liquid crystalline amides. In addition, a series of ester (non-hydrogen bonded) based monomers was also prepared and characterized. The general synthetic scheme used to prepare these materials is shown in Figure 2.

Solubilities. Rogers et al. (16-18) have prepared and reported on a large number of aromatic polyesters and polyamides containing the 2,2'-disubstituted 4,4'-biphenylene moiety. Some of the polymers were soluble in common solvents such as tetrahydrofuran and acetone, with solubility as high as 50 % in one case. The solubilities of the amide monomers synthesized in this work are shown in Table 1. These compounds exhibited virtually no solubility in common solvents such as acetone but displayed fairly high solubilities in several amide solvents, with and without added salts. Lyotropic liquid crystallinity was not observed although solubilities were as high as 40 % (w/w) in some solvents.

The solubilities of the maleimide endcapped ester based monomers were also investigated. These monomers contained unsubstituted rigid central cores. The structures of these monomers are given in Table 2. In contrast to the substituted amide monomers discussed previously, the room temperature solubilities of these unsubstituted monomers

were low, e.g. less than 5 % in 1,1,2,2-tetrachloroethane (TCE), o-dichlorobenzene, tetrahydrofuran, pyridine, p-dioxane, m-cresol, trifluoroacetic acid, and 60/40 (v/v) phenol/TCE.

Thermal Behavior. The thermal behavior of the compounds prepared in this study was investigated using a capillary melting point apparatus, hot stage polarized light microscopy, and differential scanning calorimetry. Melting was not observed for Compounds 1-3 in a capillary melting tube under normal conditions. However, the DSC trace of Compound 1 showed a sharp endotherm at approximately 340 °C, immediately followed by an exotherm as shown in Figure 3. This exotherm is presumably due to crosslinking reactions. The DSC trace of Compound 2 showed no sharp melting endotherm, but exhibited two broad endotherms in the range of 270 - 350 °C, followed immediately by a crosslinking exotherm as shown in Figure 4. Similar thermal behavior has been attributed to a retro Diels-Alder reaction of the two conformational isomers of the nadimide group (19). The retro Diels-Alder reaction results in the formation of cyclopentadiene and a maleimide endgroup. This reaction is followed by several possible crosslinking or addition reactions. Compound 3 exhibited similar behavior.

These monomers were also examined at very high heating rates. If the capillary melting apparatus or the microscope hot stage was heated to 350 °C prior to inserting the sample, Compound 1 melted, flowed, and solidified within a few seconds. Solidification was assumed to be due to polymerization and crosslinking. Liquid crystalline phases were not observed for Compound 1. However, when Compound 2 was subjected to this same experiment the sample melted into a nematic phase. The sample crosslinked in the nematic phase after approximately ten seconds and the nematic texture was preserved in the solid state. Compound 3 showed similar behavior when placed on a preheated microscope hot stage at 340 °C. This melting behavior can be explained if reaction occurred in the solid state during heating of the sample. At slow or normal heating rates, partial reaction of the monomer can occur below the crystalline melting point and prevent the material from flowing. At very high heating rates, melting and crosslinking (solidification) are observed in rapid succession.

A series of ester based maleimide endcapped monomers was also synthesized. These monomers are shown in Table 2. The DSC traces of the ester based monomers showed sharp endotherms in the range of 270 - 300 °C, followed immediately by a crosslinking exotherm. A representative trace is shown in Figure 5. The monomers melted into a nematic liquid crystalline phase and crosslinked shortly after melting. The nematic texture was retained in the crosslinked solid state. Melting was not always observed at low heating rates but was observed at lower heating rates than the amide based monomers. As described earlier, this may be due to partial reaction in the solid state during the heating cycle.

### Conclusions

Rigid rod thermoset molecules were prepared by combining rigid, rodlike central units, similar to those found in LCP's, with well known crosslinking functionalities. The initial results have shown that liquid crystalline phases were obtained in these types of materials. The thermal polymerization of these monomers was conducted in the nematic phase and the nematic order was preserved in the crosslinked solid. Melting temperatures for the monomers reported here were high and this limited the time available in the fluid state. Crosslinking usually occurred within seconds after melting. Future efforts will concentrate on complete characterization of the monomers discussed herein and on the synthesis and characterization of additional rigid, rodlike thermosetting monomers with improved processability.

### Acknowledgements

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## Literature Cited

1. Roviello, A.; Sirigu, A. J. Polym. Sci., Polym. Lett. Ed., 1975, 13, 455.
2. Calundann, G.W.; Jaffe, M. Proc. Robert A. Welch Foundation, 1983, p. 247.
3. Jackson, Jr., W.J.; Kuhfuss, H.F. J. Polym. Sci., Polym. Chem. Ed., 1976, 14, 2043.
4. Chemical Business, April 1989, pp. 44-6.
5. Finkelmann, H.; Kock, H.J.; Rehage, G. Makromol. Chem., Rapid Commun. 1981, 2, 317.
6. Conciatori, A.B.; Choe, E.W.; Farrow, G. U.S. Patent 4 440 945, 1984.
7. Conciatori, A.B.; Choe, E.W.; Farrow, G. U.S. Patent 4 452 993, 1984.
8. Conciatori, A.B.; Choe, E.W.; Farrow, G. U.S. Patent 4 514 553, 1985.
9. Calundann, G.W.; Rasoul, H.A.A., Hall, H.K. U.S. Patent 4 654 412, 1987.
10. Stackman, R.W. U.S. Patent 4 683 327, 1987.
11. Rao, B.S. J. Polym. Sci., Part C: Polym. Lett. 1988, 26, 3.
12. Adams, R.; Ulich, L.H. J. Am. Chem. Soc. 1920, 42, 599.
13. Jackson, Jr., W.J. Br. Polym. J. 1980, 12, 154.
14. Kwolek, S.L.; Morgan, P.W.; Schaefgen, J.R. In Encyl. Polym. Sci. Eng.; Wiley: New York, 1987; Vol. 9, p 1.
15. Gaudiana, R.A.; Minns, R.A.; Sinta, R.; Weeks, N.; Rogers, H.G. Prog. Polym. Sci. 1989, 14, 47.
16. Rogers, H.G.; Gaudiana, R.A.; Hollinsed, W.C.; Kalyanaraman, P.S.; Manello, J.S.; McGowan, C.; Minns, R.A.; Sahatjian, R. Macromolecules 1985, 18, 1058.
17. Sinta, R.; Gaudiana, R.A.; Minns, R.A.; Rogers, H.G. Macromolecules 1987, 20, 2374.
18. Sinta, R.; Minns, R.A.; Gaudiana, R.A.; Rogers, H.G. J. Polym. Sci., Part C: Polym. Lett. 1987, 25, 11.
19. Wong, A.C.; Ritchey, W.H. Macromolecules 1981, 14, 825 and Wong, A.C.; Garroway, A.N.; Ritchey, W.H. Macromolecules 1981, 14, 832.

## List of Figure Captions

Figure 1. Schematic diagram of LCT concept.

Figure 2. Synthetic scheme for rigid rod monomers.

Figure 3. DSC trace of Compound 1. Heating rate, 20 °C min<sup>-1</sup>.

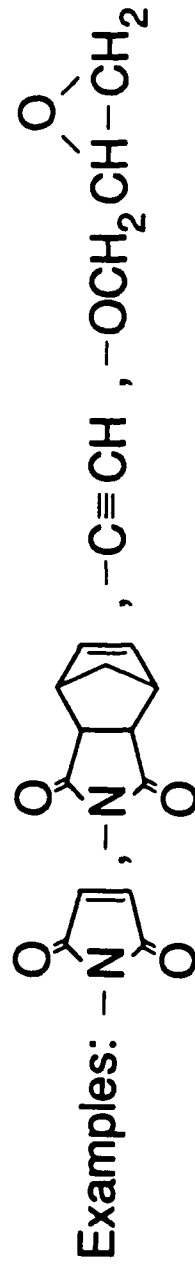
Figure 4. DSC trace of Compound 2. Heating rate, 40 °C min<sup>-1</sup>.

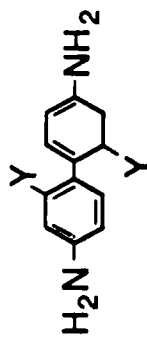
Figure 5. DSC trace of Compound 4. Heating rate, 20 °C min<sup>-1</sup>.

# LIQUID CRYSTAL THERMOSET CONCEPT

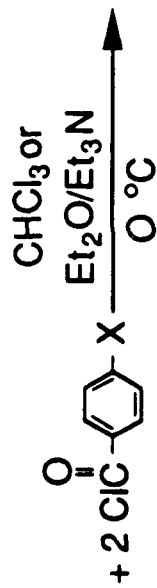


X = Conventional crosslinking group



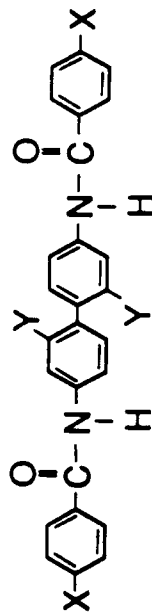


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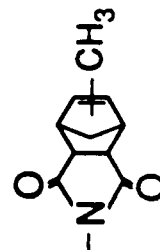
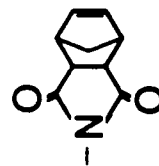
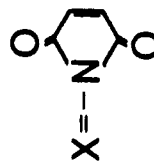
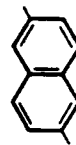
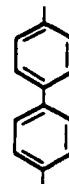
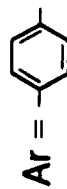
CHCl<sub>3</sub> orEt<sub>2</sub>O/Et<sub>3</sub>N

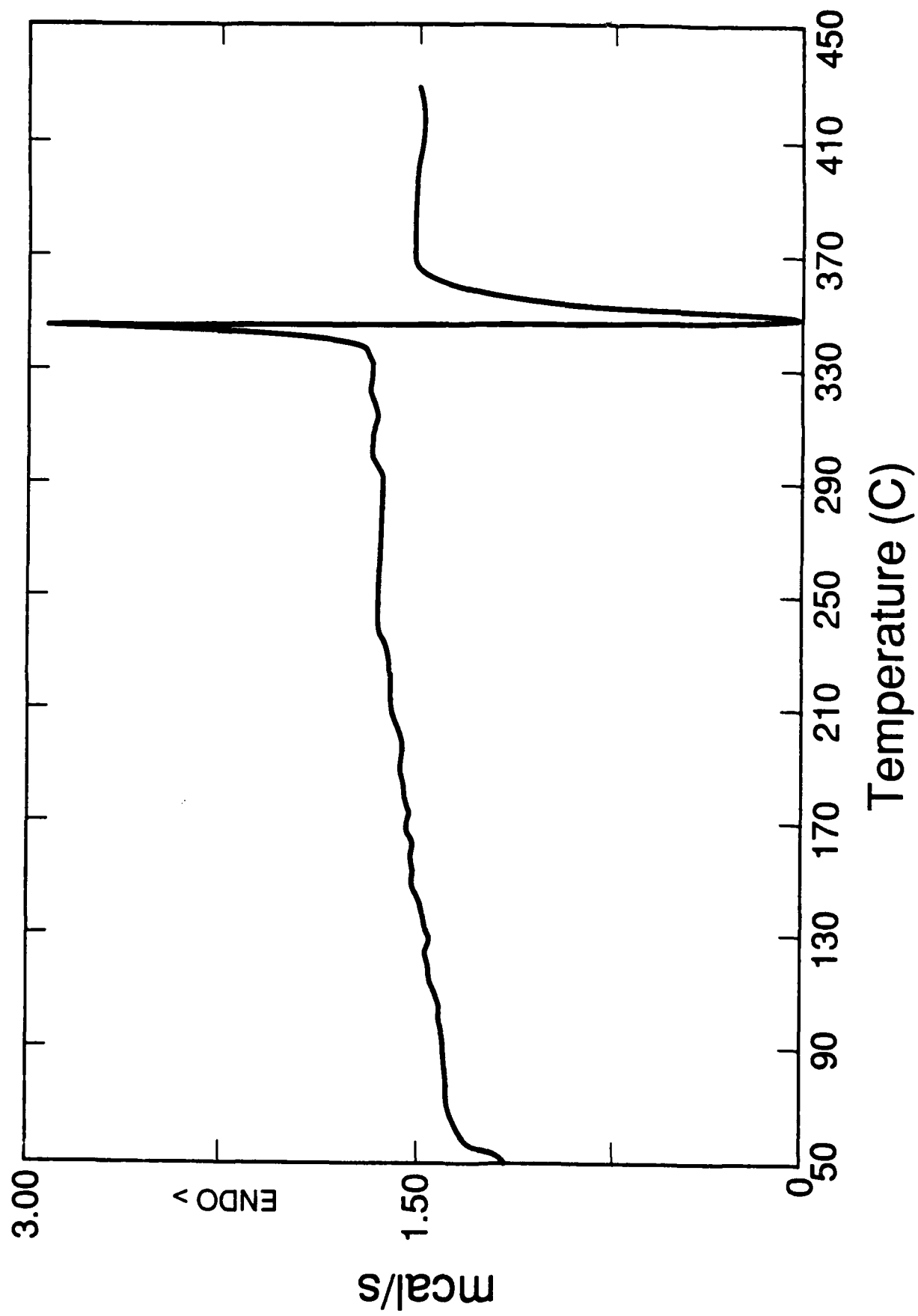
0 °C

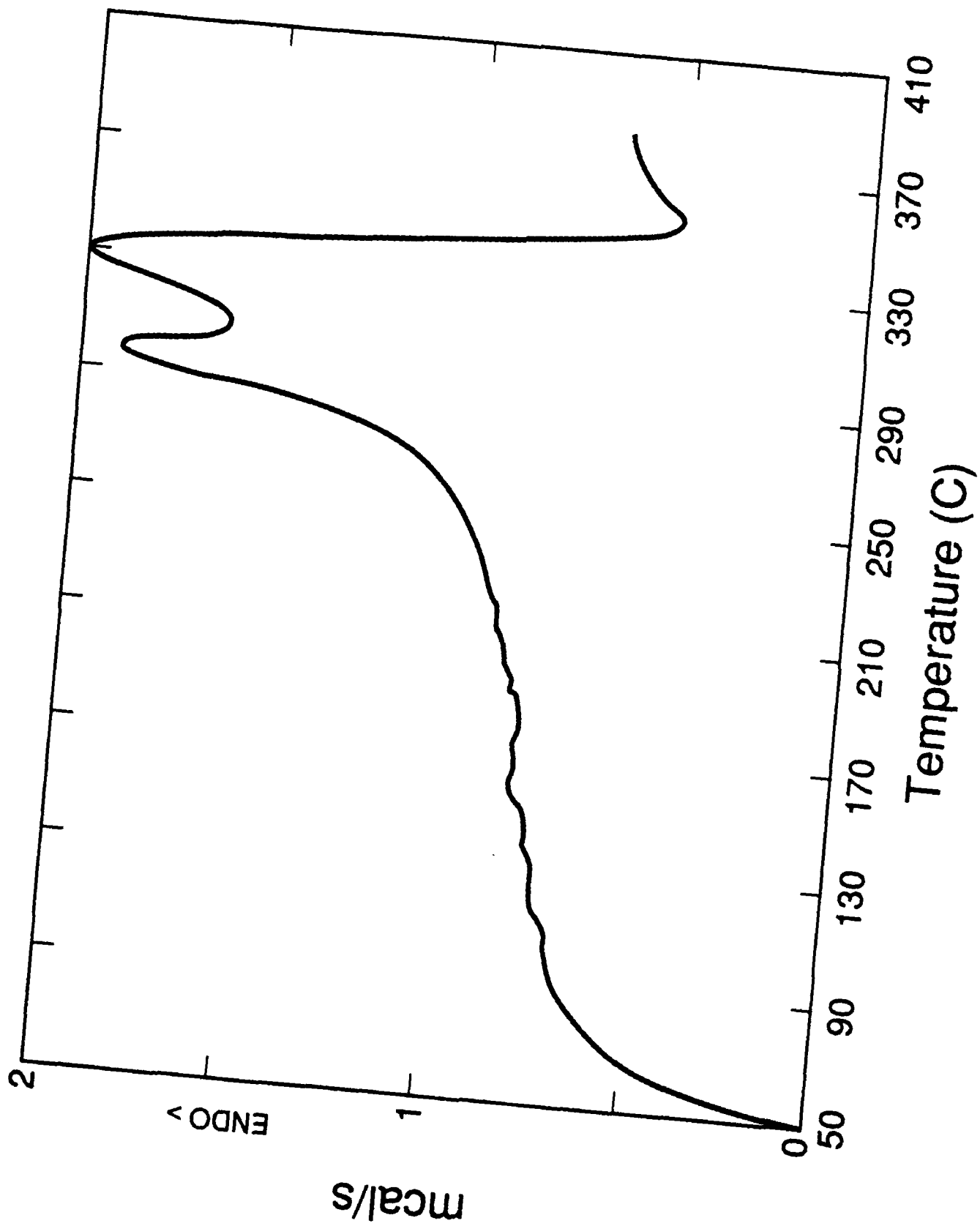
OR



HO-Ar-OH

Y = -CH<sub>3</sub>





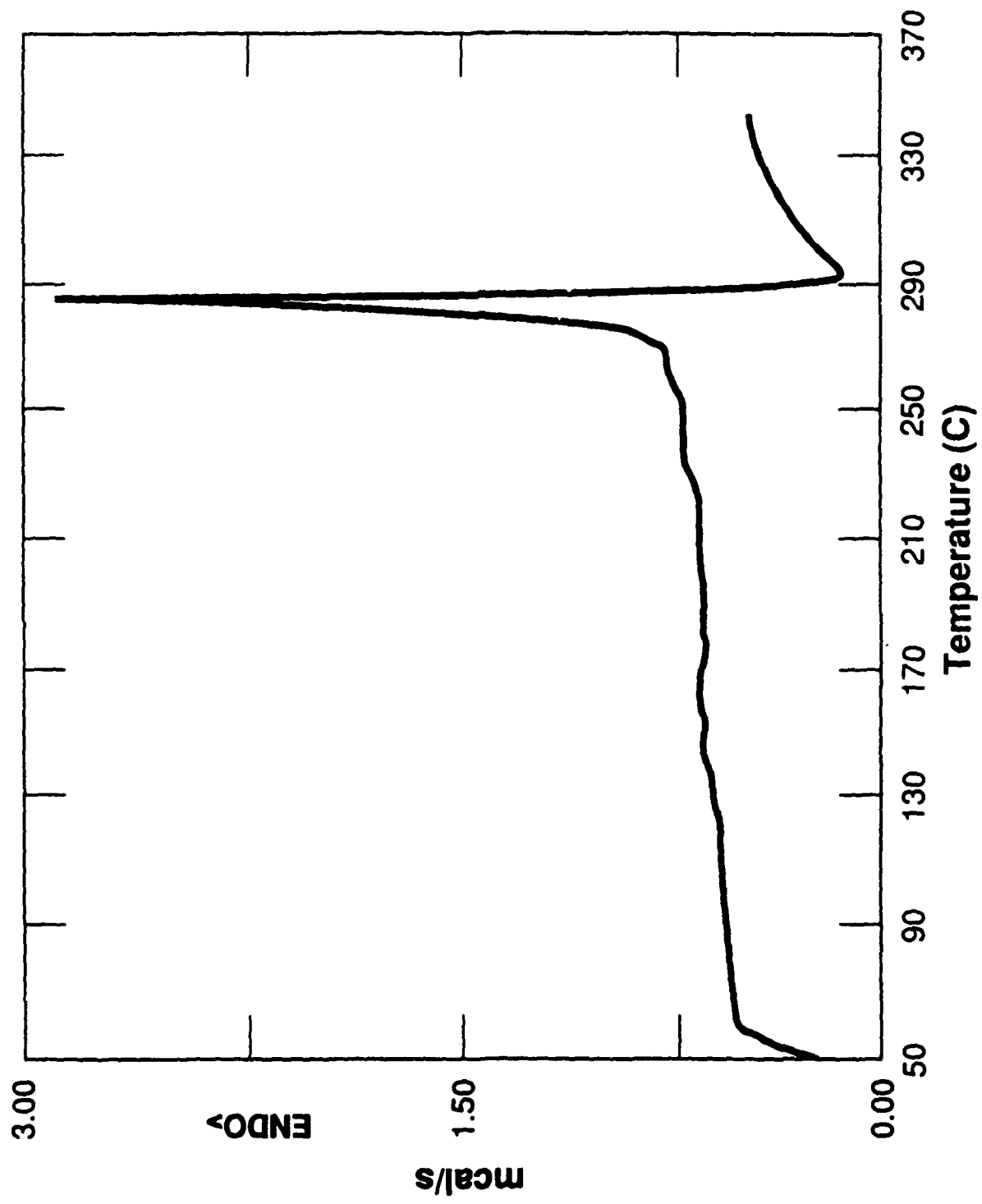
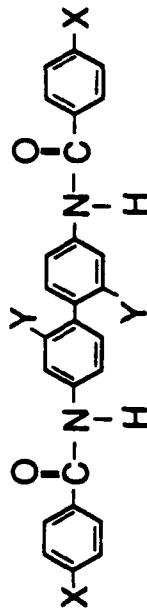


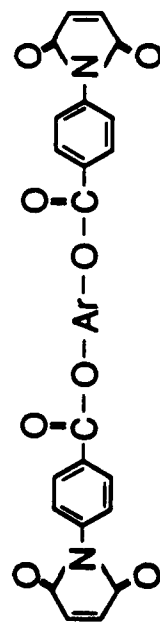
Table I. Room Temperature Solubilities of Amide Monomers



COMPOUND	X	Y	$T_m, ^\circ\text{C}$	SOLUBILITY, % (w/w)			
				DMAC	DMAC/LiCl	DMF	NMP
1		$\text{CH}_3$	>350	<20	30-40	<20	20-30
2		$\text{CH}_3$	>350	20-30	30-40	<20	25-30
3		$\text{CH}_3$	>350	<20	>40	<25	20-30

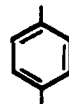


Table II. Thermal Transitions of Bismaleimide Monomers



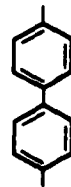
Compound	Ar	$T_m, ^\circ\text{C}^a$
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4



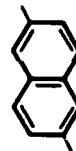
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<sup>a</sup> Melting point determined by DSC, reported as extrapolated onset.

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